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Hollow cathodes featuring C12A7 electride as a low work function thermionic emitter are hypothesized to have faster start-up times and lower operating temperatures than conventional hollow cathodes. C12A7 electride is a crystalline ceramic in which electrons clathrated in subnanometer sized cages act as a conductive medium. This unique structure leads to an extremely low work function. Calculations predict equivalent levels of current emission as LaB6 or CeB6 hollow cathode inserts, but at a much lower temperature. C12A7 electride is stable at temperatures below its re-crystallization temperature (~1000 □C) and is not consumed during operation. C12A7 electride has been fabricated at CSU using a simplified, one-step approach that results in a more conductive material than previously reported. Hollow cathodes have been designed at CSU that take advantage of the unique properties of C12A7 electride, and are capable of starting at room temperature without the benefit of a heater. The C12A7 electride hollow cathodes have been shown to run stably in a diode configuration at low flow rates. In addition, a C12A7 electride hollow cathode successfully operated with a 6 kW hall thruster, producing an efficiency comparable with that of a traditional LaB6 hollow cathode. Our paper will present the results obtained from these recent tests. In addition, surface studies analyzing the effect of cathode operation on the C12A7 electride surface will be discussed.

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C12A7 ELECTRIDE HOLLOW CATHODE

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ABSTRACT

Hollow cathodes featuring C12A7 electride as a low work function thermionic emitter are hypothesized to have faster start-up times and lower operating temperatures than conventional hollow cathodes. C12A7 electride is a crystalline ceramic in which electrons clathrated in sub-nanometer sized cages act as a conductive medium. This unique structure leads to an extremely low work function. Calculations predict equivalent levels of current emission as LaB6 or CeB6 hollow cathode inserts, but at a much lower temperature. C12A7 electride is stable at temperatures below its re-crystallization temperature (~1000 °C) and is not consumed during operation. C12A7 electride has been fabricated at CSU using a simplified, one-step approach that results in a more conductive material than previously reported. Hollow cathodes have been designed at CSU that take advantage of the unique properties of C12A7 electride, and are capable of starting at room temperature without the benefit of a heater. The C12A7 electride hollow cathodes have been shown to run stably in a diode configuration at low flow rates. In addition, a C12A7 electride hollow cathode successfully operated with a 6 kW hall thruster, producing an efficiency comparable with that of a traditional LaB6 hollow cathode. Our paper will present the results obtained from these recent tests. In addition, surface studies analyzing the effect of cathode operation on the C12A7 electride surface will be discussed.

INTRODUCTION

Hollow cathodes are the primary electron source in space propulsion applications, as well as in many ground-based devices such as gaseous lasers and plasma processing sources**.** They are often preferable to filament sources due to their increased robustness and lifetime. Hollow cathodes are cylindrical in shape, and consist of an orificed tube with a low work function material along in the inner surface (Goebel & Katz, 2008) (Polk, Goebel, et al, 2006). The ease with which the electrons are emitted off the insert is related to the work function of the material (Coulombe & Meunier, 1997) (Murphy & Good, 1956) (Paulini, et al, 1993). Lower work function indicates equivalent emission can be obtained at lower temperatures, improving the power efficiency because lower temperature cathodes lose less heat. An ultra low temperature cathode has the potential to be extremely efficient and could be fabricated from inexpensive materials instead of refractory metals.

$12CaO\text{-}7Al_2O_3$, or C12A7 in material science parlance, is a novel material found to have properties uniquely suited to electron emission when in the electride form. The low work function of C12A7 electride derives from its unique structure. The calcium aluminate phase is one of

several alumina-lime phases found in common alumina-based cements. C12A7 has a naturally formed nanostructure, in which subnanometer-sized cages form a three-dimensional crystal lattice, as shown in Figure 1. The unit cell consists of twelve cages. Although this cage structure is similar to those found in clathrate phases of ice and in zeolites, there is an important difference in that the unit cell of C12A7 is positively charged. In other words, there are four fewer electrons on the atoms that comprise the framework cage of C12A7 than are needed to neutralize the cage. Interestingly, the positive charge is counteracted by two atomic oxygen ions (O^{2-}) that are clathrated (floating) within two of the twelve subcages. New properties can be imparted to C12A7 if the free oxygen ions are substituted with anions like O^- and H^-, but especially interesting features are possible when four electrons are substituted for the two O^{2-} ions to form C12A7 electride, the first and to date only inorganic electride discovered that is stable at high temperature (Matsuishi, et al., 2003) (Kim, Matsuishi, et al, 2007). The stability of the C12A7 electride is attributable to the unique cage structure as well as the fully oxidized nature of the lattice.

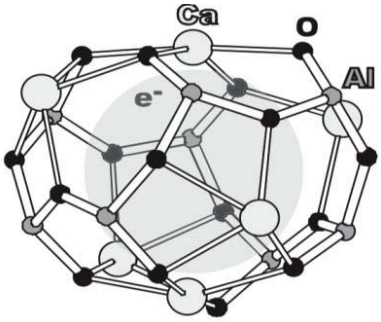

Figure 1: Structure of C12A7 electride in which an electron is clathrated within the positively charged lattice framework (Toda, et al., 2007).

The work functions of current state-of-the-art hollow cathode insert materials lanthanum hexaboride (LaB6) and cerium hexaboride (CeB6) are near 2.7 eV, while the work function of barium-impregnated porous tungsten (Ba-W) is near 2.1 eV (Goebel, Watkins, & Jameson, 2007). LaB6 and CeB6 are generally heated to approximately 1900 K to obtain sufficient levels of emission, while Ba-W is heated above 1300 K (Goebel, Watkins & Jameson, 2007). These temperatures require well-made heaters and good thermal insulation. Ba-W cathodes, while operating at lower temperatures, are more susceptible to both poisoning and high rates of evaporation if operated at high current (Goebel, Watkins & Jameson, 2007). In contrast, the work function of C12A7 electride has been measured in field emission tests to be as low as 0.6 eV, due to its unique charged lattice structure (Kim, Toda, et al, 2006) (Medvedeva, Teasley, & Hoffman, 2007) (Toda, et al., 2004). If the 0.6 eV work function could be achieved and maintained, a C12A7 cathode would theoretically operate at only ~400 K.

FABRICATION

In 2010, C12A7 electride was fabricated in the CSU CEPPE Laboratory in a one-step procedure (Rand, Qian, & Williams, 2010) (Rand, Hoyt, & Williams, 2011). A vacuum tube furnace capable of reaching temperatures of 1800 °C was constructed. Two precursors ($CaCO_3$ and Al_2O_3) were mixed in a 12:7 stoichiometric ratio and carefully ground with a mortar and pestle to minimize the crystal size and help facilitate a solid-state reaction. The mixture was heated to 1600 °C in a carbon crucible fabricated from fine-grained graphite. The carbon crucible was found to be necessary for the successful formation of C12A7 electride. Although the exact mechanism is unknown, it is thought that the carbon crucible is needed to supply carbon anions to occupy the subcages and permit the formation of the lattice, which then evacuate upon cooling leaving behind their electrons (Kim, Toda, et al, 2006).

(a)  (b) 

Figure 2: Fabricated C12A7 electride formed (a) on a graphite crucible substrate at 1600 °C, broken open for illustration and (b) in a graphite crucible at 1700 °C.

EXPERIMENTAL RESULTS AND DISCUSSION

FIRST GENERATION PROTOTYPE

Given the ease with which C12A7 electride could be formed on graphite, the first generation prototype hollow cathode was fabricated from graphite and designed to utilize C12A7 electride as an insert. The cathode barrel was a hollow graphite tube with a 1.25 mm diameter orifice. The cathode was filled with the chemical precursors and placed directly in the vacuum furnace, in order to melt the precursors to its inner surface. Once the insert was melted to the barrel, the barrel was mounted on a graphite bulkhead that allowed for electrical connections, mounting for the keeper, and a gas supply to the barrel. The keeper was also made out of graphite, had a 2.54 mm diameter orifice, and was mounted 1.25 mm away from the barrel end.

The cathode was mounted approximately 15 cm away from a ring anode. In addition to the gas feed going into the cathode barrel, a second feed line was used to raise the chamber pressure. No heater was used to heat the cathode barrel. A plasma was ignited through an arc discharge method, by which a bias was applied between the keeper and the barrel. Due to the lack of a heater, there was no lengthy start-up process, and the cathode could be ignited almost immediately especially when it was first used. Given the interest in fast-starting cathodes (Rubin & Williams, 2008), this feature is very promising. In some instances during starting and re-starting the cathode, several sparks between the keeper and barrel were observed before a stable plasma discharge was sustained. The degree of difficulty in starting was directly correlated to the number of hours the cathode had been operated.

Even at its most stable, the first generation prototype cathode discharge was prone to extinguishing or “winking” out (the probability of which was directly related to the number of hours the cathode had been operated). When running, the cathode switched between different modes of operation that were apparent to the eye, sometimes running cleanly and other times erratic with ejected material.

A first generation C12A7 electride hollow cathode prototype was operated in conjunction with a 6 kW Hall thruster at the Air Force Research Laboratory. The cathode was placed in the plane of the thruster exit, approximately 5 cm from the thruster edge, facing downstream. The thruster anode and gas flow were turned on prior to the cathode starting. The cathode was started by the arc discharge method used previously. The thruster ran for approximately 30 minutes before the cathode winked out for the first time. The cathode discharge was restarted several times. After multiple restarts, a bridge of graphite developed between the keeper and the cathode barrel, which shorted the keeper to the cathode and prevented any further restarts.

SECOND GENERATION PROTOTYPE

A second generation C12A7 electride hollow cathode prototype was designed in an effort to improve operation stability and extend lifetime (Figure 3). The graphite barrel was replaced with a 6.3 mm swaged tantalum tube. The swaged snout was grinded back to produce a 0.1 mm diameter orifice. Two external tantalum wire keepers replaced the enclosed graphite keeper of the first generation prototype. One keeper was placed very close to the orifice and was used to spark the arc discharge. The second was placed further downstream and functioned as a "sustaining keeper" to stabilize operation once the cathode was running. Two separate keepers were necessary to simplify the power supply connection scheme and prevent application of high voltage to the sustaining keeper power supply. A thermocouple was placed on the exterior surface of the barrel at the downstream end to monitor the temperature.

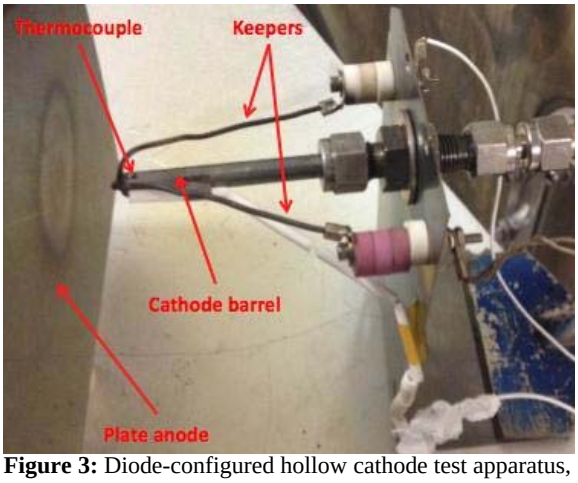

Figure 3: Diode-configured hollow cathode test apparatus, with cathode barrel thermocouple.

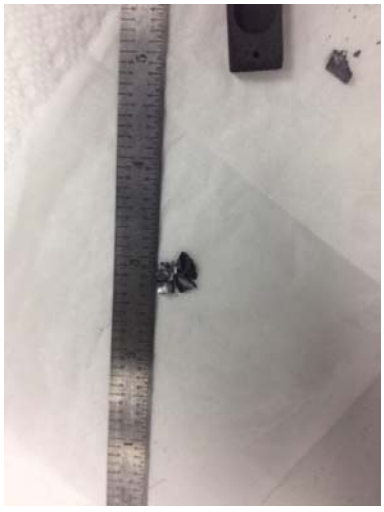
Figure 4: C12A7 electride insert pieces for a second generation prototype hollow cathode.

Because the cathode barrel was no longer graphite, C12A7 electride could not be formed directly on the inner surface. Instead, the precursors were heated in a rectangular graphite crucible, which was then fractured into small pieces. Segments that were small enough to fit in the barrel tube and were mostly comprised of C12A7 electride were selected as insert pieces (Figure 4). Several pieces were used in each run as the insert.

The cathode was tested in a diode configuration with a plate anode located approximately 5 cm downstream of the orifice. Like the first generation prototype, it started after only several arc discharges. However, the operation was a great deal more stable, sometimes varying less than 0.1 V/min, and there was no material ejected (Figure 5).

Operating temperatures as low as 990°C were observed. However, during some experiments, the temperature was found to fluctuate by as much as several hundred degrees at a constant operational set point. This variation was suspected to be caused by the discontinuous nature and uncontrolled placement of the insert surface pieces.

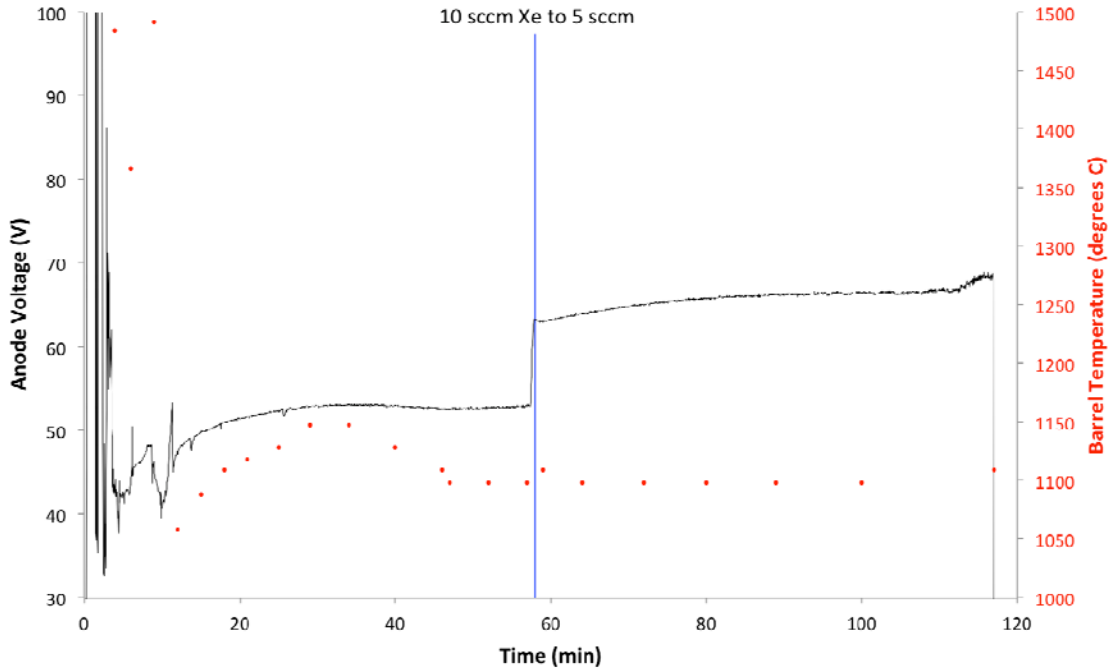

Figure 5: Stable operation of a second generation prototype. The discharge current was 4 A, and the keeper current was 0.5 A. The high anode voltage is due to both the lack of radiation shielding on the cathode and an insulating layer on the anode surface.

In general, it was found that insert pieces that had been run in the cathode previously did not operate as well. This was exhibited in higher anode voltages, less stable operation, and higher operating temperatures. There appeared to be no detrimental effects when an insert piece was left in atmosphere for several weeks prior to operating in the cathode.

THIRD GENERATION PROTOTYPE

The third generation electride hollow cathode prototype was designed to address the poor operation after the first run observed in the second generation prototype. A second generation prototype cathode was cut open and examined following several hours of operation. It was found that the C12A7 electride material had melted and spread across the inside surface of the tube. Additionally, the coating was no longer conductive. Kim, Toda, et al, 2006, discusses the conversion of C12A7 electride to the insulative eutectic (CA+C3A) when heated to a high temperature and cooled without the presence of a template anion (supplied by the graphite crucible in the original formation process). Tantalum has not been shown to be a source of the template anions needed for the formation.

To keep the C12A7 electride material in its conductive form, a graphite sleeve was integrated in the third generation prototype. It was fabricated from the same fine-grained graphite species as the crucibles, and extended 2.54 cm down the hollow cathode barrel from the orifice plate. C12A7 electride material was cut from the fabrication crucible using a diamond saw in a strip approximately 2.5 mm wide and 13 mm long. The insert was fabricated using this new method in an effort to produce a continuous emission surface of reproducible surface area that could be easily positioned in the cathode.

Tests are ongoing, but initial tests indicate that the graphite sleeve may lead to cathodes that can be operated multiple times. Figures 6 and 7 show consecutive operations of the third generation prototype with a single insert. The chamber was vented between the runs. The cathode was operated at 3 A of discharge current, and the gas flow was varied as indicated on

the graphs. The anode voltage decreased on the second run due to the removal of an insulating contamination layer on the plate anode.

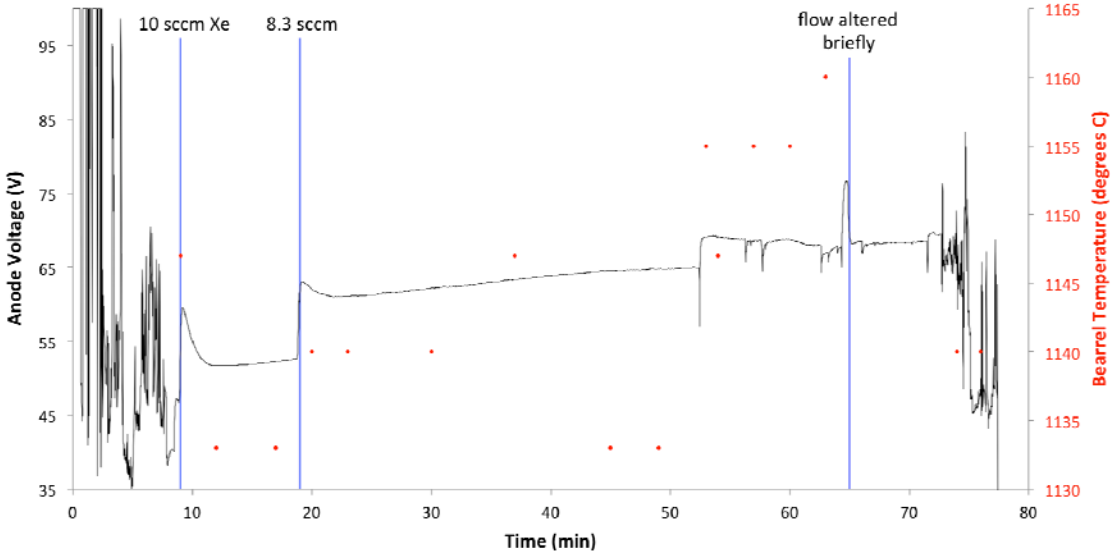

Figure 6: First operation of a third generation prototype cathode. The discharge current was 2.5 A, and the keeper current was 0.5 A. The high anode voltage is due to both the lack of radiation shielding on the cathode and an insulating layer on the anode surface.

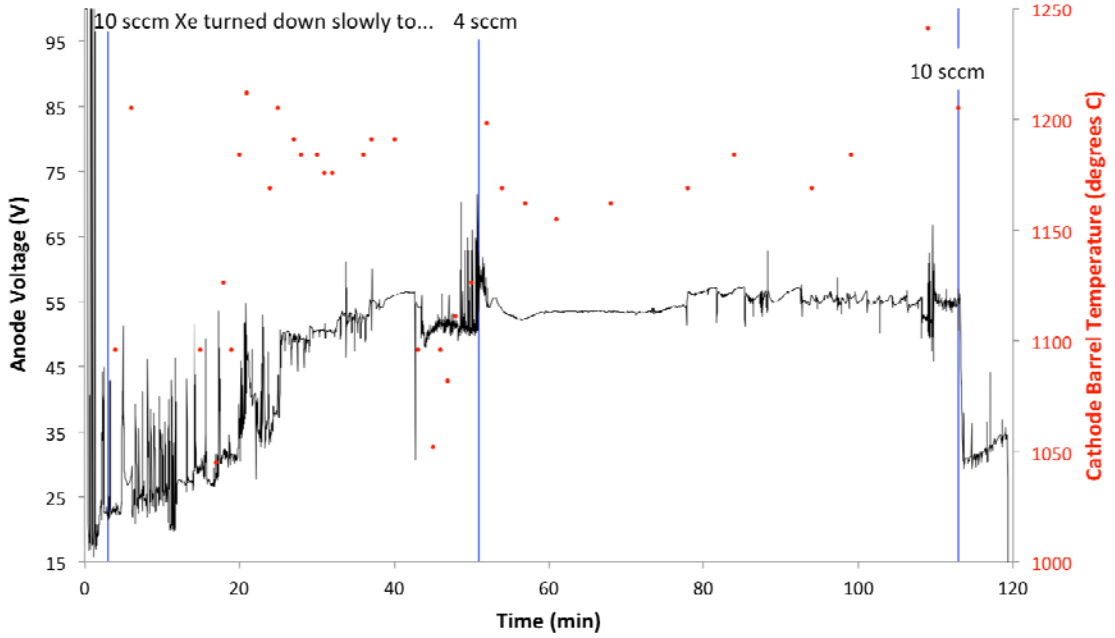

Figure 7: Second operation of a third generation prototype cathode. The discharge current was 2.5 A, and the keeper current was 0.5 A. The lower anode voltage is due to the removal of the insulating coating on the anode.

SUMMARY AND CONCLUSIONS

C12A7 electride has several properties that make it a promising candidate for hollow cathode inserts. Its durability and low work function allow for an instant start-up through the arc discharge method. The inherent stability of the compound dramatically reduces its sensitivity to

poisoning relative to state-of-the-art insert materials, and the nontraditional method of conduction allows for operation without consumption of the insert material. A first generation hollow cathode prototype operating with a C12A7 electride insert was successfully operated in conjunction with a laboratory Hall thruster for approximately 30 minutes before a short between the cathode and keeper electrode rendered it inoperable. A second generation prototype was successfully operated before it gradually degenerated, exhibiting instability and difficulty relighting. A modification involving the use of a graphite sleeve inside the cathode barrel shows promise in initial testing. Future work will involve additional restart capability analysis, longer duration tests and the use of radiation shielding in an attempt to increase power efficiency.

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